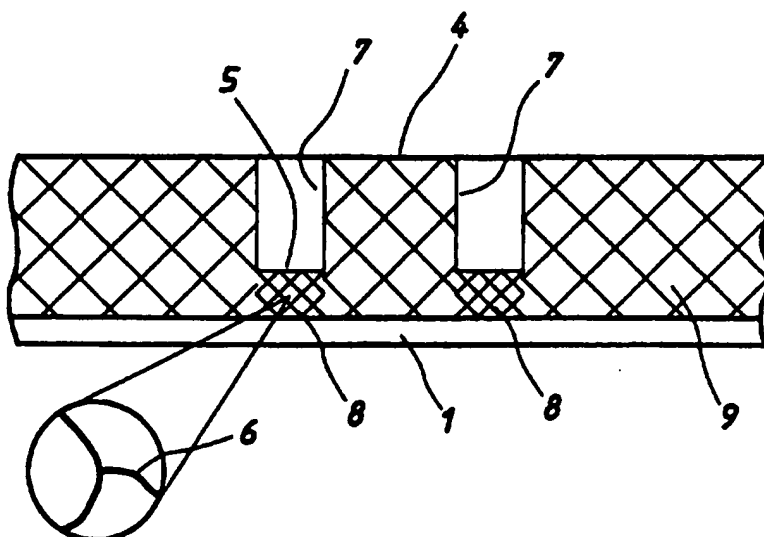




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: DEFINING AN ELECTRODE AREA**(57) Abstract**

The present invention relates to a method for defining an area (4) of a layer on a porous substrate comprising compressing a volume of the substrate to produce a compressed region (8) which defines, or which in combination with an edge (7) of the substrate or of the layer defines, a boundary of the area and which substantially prevents the transport of material through or across its surface. The present invention also relates to an electrochemical sensing device comprising: a porous substrate; and an electrode (1) on one side of the substrate; wherein a region of the substrate is compressed to an extent which forms a barrier to migration of electrolyte within the substrate, the compressed region defining, or in combination with an edge of the substrate or the electrode defining, a zone on the electrode of predetermined area.

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DEFINING AN ELECTRODE AREA

TECHNICAL FIELD:

The present invention relates to a method for defining an area of a coating or layer attached to or in contact with a porous substrate. More particularly, the present invention relates to a method wherein the coating or layer is an electrode. Although
5 the invention will be described with reference to its application in the electrochemical area it is not intended that the invention be limited to that use. It may extend to any application where a defined area of a porous substrate is required.

BACKGROUND ART:

10 In the past it has been found that whenever quantitative electrochemical measurements are performed it is necessary to have both a reproducible and accurately defined electrode area which is in contact with the sample being analysed. When performing a measurement in a bulk solution the usual practice has been either to have the electrode immersed to a certain level in the liquid or alternatively to have an
15 insulation layer applied to the electrode to leave only a precisely defined area in

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contact with the solution. These practices have proved to be relatively expensive and unreliable. It has also been found that when these methods are used it is difficult to prevent leakage and contact with the electrode outside the defined area, especially when the substrate upon which the electrode is placed is porous.

5 The present invention seeks to overcome or at least ameliorate the problems of the prior art by providing a method which is inexpensive, simple to apply and reliable.

SUMMARY OF THE INVENTION:

 According to one aspect the present invention consists in a method for defining an area of a layer on a porous substrate comprising compressing a volume of the
10 substrate to produce a compressed region which defines, or which in combination with an edge of the substrate or of the layer defines, a boundary of the area and which substantially prevents the transport of material through or across its surface.

 According to a second aspect the invention consists in an electrochemical sensing device comprising:

15 a porous substrate; and
 an electrode on one side of the substrate; wherein a region of the substrate is compressed to an extent which forms a barrier to migration of electrolyte within the substrate, the compressed region defining, or in combination with an edge of the substrate or the electrode defining, a zone on the electrode of predetermined
20 area.

 According to a third aspect the porous substrate of the second aspect is a membrane that is permeable to a fluid containing a first species to be analysed but substantially impermeable to a second species contained in the fluid, the second

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species being of a kind which would interfere with electrochemical sensing of the first species.

Preferably, the layer, which may be attached to or in contact with the porous substrate or may be a coating applied to the substrate, is an electrode and the area
5 being defined is an electrode area. When the layer is an electrode it is usually sputter deposited on the surface of the substrate so as to form a continuous film on the surface. However, other methods such as electroless plating, electroplating, evaporation, anodization or the like can be used to form the electrode. Usually the film thickness on the substrate is 10-200nm, more preferably 60-120nm.

10 Materials which would be suitable as an electrode include gold, silver, platinum, palladium, iridium, lead, and alloys of those metals, carbon, carbon mixed with a binding material, and silver partially covered with a porous layer of an insoluble silver salt such as silver chloride, silver bromide, silver iodide, silver ferricyanide and silver ferrocyanide. In electrochemical sensing devices according to
15 the invention there will typically be two or more electrodes and these may be disposed on one side of the substrate or on opposite sides of the substrate.

In a preferred form the resulting substrate produced from the method of the invention will have at least two discrete regions - one region being compressed and the other region being uncompressed. This resulting substrate has been found to be
20 particularly useful when used as an electrochemical sensing device. When a sample is placed on the uncompressed region of the resulting substrate, migration of the sample to another region of that substrate, being divided from the first region by the compressed region, is substantially prevented. It has been found that the sample is

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confined to a predetermined area of the resulting substrate and therefore to a predetermined area of the electrode attached to or otherwise in contact with the resulting substrate.

The method of the present invention works by substantially eliminating or
5 sufficiently constricting the porous structure of the substrate in the compressed region to render that region effectively impermeable.

The method of the present invention can be used alone or preferably, in conjunction with a blocker. A blocker, in the present invention, is a substance which is placed in the substrate such that it does not prevent the transport of material in the
10 uncompressed regions of the substrate but assists in preventing transport of material in the compressed areas. Examples of material suitable as a blocker may include glucose, agar, gelatine, starch or the like.

In a preferred form the blocker is conveniently loaded into the precompressed porous substrate using the steps of:

- 15 (a) dissolving the blocker in a suitable solvent;
(b) wetting the substrate with the solution of the blocker; and then
(c) removing the solvent by evaporation.

In another preferred form the porous substrate is of a kind having pores which increase in diameter from a smooth or shiny side to a rough side. The porous substrate
20 is desirably of the kind disclosed in U.S. Patent Nos 4,629,563 and 4,774,039 both of which are incorporated herein in their entirety by reference. However according to end use the substrate may be an asymmetric or symmetric membrane.

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The substrate may be any suitable porous material that is compressible and which will maintain its mechanical integrity during compression. Examples of such materials include polymers or mixtures of polymers such as polysulfones, polyvinylidene halides such as polyvinylidene difluorides, tetrafluoroethene, 5 polyamides, polyimides, polyethylenes, polypropylenes, polyacrylonitriles, polycarbonates or the like. The materials may be in the form of a sheet, tube or hollow fibre which have microscopic or macroscopic pores.

The thickness of the substrate is selected with the end use in mind. Usually it is desirable for the substrate to be thin to minimise sample volume. However, 10 sufficient thickness is required to provide mechanical strength for handling and to maintain sufficient separation between electrodes on opposite faces of the substrate to prevent electrical short circuits.

In some applications for example anodic stripping, larger sample volumes and greater thickness will be preferred. Preferred embodiments and illustrative examples 15 of the present invention will now be described, by way of example only, with reference to the accompanying figures, in which:-

BRIEF DESCRIPTION OF THE FIGURES:

Figure 1 shows a cross-sectional view of a microporous substrate in uncompressed form, with a portion shown as an enlarged image;

20 Figure 2 shows the substrate of Figure 1 with compressed regions in combination with the edge of the microporous substrate to define a perimeter of the area with a portion of the compressed region shown as an enlarged image;

Figure 3 shows a top view of the substrate of Figure 2;

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Figure 4 shows an end view of the substrate of Figures 1 or 2;

Figures 5 is similar view to Figure 1 where a blocker has been added to the substrate;

Figure 6 is a similar view to Figure 2 where a blocker has been added to the
5 substrate;

Figures 7 is a top view of one embodiment differing in respect of defined target areas;

Figure 8 is a top view of a second embodiment differing in respect of target areas;

10 Figure 9 is a top view of a third embodiment differing in respect of target areas;

Figure 10 is a top view of a fourth embodiment differing in respect of target areas; and

Figure 11 shows a top view of a preferred embodiment of the invention.

15 Figure 1 illustrates a microporous substrate 10 in an uncompressed form having an electrode 1 being attached to or in contact with substrate 10. The thickness of the precompressed substrate is preferably about 180 μ m, more preferably from 30-150 μ m. The pore size ranges from 10 kilodaltons cut-off (lower limit) to 5 microns and preferably from 0.1 μ m to 0.8 μ m, more preferably from 0.2 μ m to 0.5 μ m. Also
20 shown in Figure 1 is the magnified image which shows the uncompressed pores 2 of the substrate. When pressure is applied to an area 5 of the microporous substrate 10, one or more discrete compressed regions 8 are produced. As shown in Figure 2 and 3 the compressed regions 8 in combination with the edges 7 of the uncompressed region

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define a boundary of the area 4. This compressed region 8 substantially prevents the transport of material (not shown) through or across its volume.

The magnified image of Figure 2 shows the pores 6 of region 8 which have been compressed so as to substantially prevent transportation of material across or
5 through region 8.

Figures 5 and 6 illustrate the effect of the addition of a blocker 3. As shown in the magnified image of Figure 6 the addition of blocker 3 makes the blockage of the pores 6 in region 8 more complete so as to prevent the transportation of material across or through it.

10 Figures 7 and 8 illustrates the compressed area 5 being in the shape of a ring or square on one side of substrate 10 and overlying an electrode 1 on the opposite side. The compressed region 8 defines a boundary of an area 4 of the electrode and which substantially prevents the transport of material (not shown) through or across region 8 to adjoining regions 9.

15 Although not illustrated in the drawings the area 4 of electrode 1 may be defined partly by compressed region 8 or region 5 and partly by an electrode edge.

Figure 9 shows a rectangular area 4 being defined on one edge by compressed substrate 5 and on the other edges by the edge 11 of uncompressed substrate 9.

Figure 10 shows a rectangular area 4 being defined by two compressed regions
20 5 in combination with two edges 11 of uncompressed substrate 9.

In the present invention the porous substrate is preferably pressed by means of a press or any suitable compressing process which will allow for at least one region of the porous substrate to be compressed. The amount of pressure to be applied varies

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between substrates, at both the high and low end of the pressure range. It is preferred that a sufficient amount of pressure is applied to the substrate which will collapse the pore structure of the substrate to achieve substantial non-porosity, but not too high so as to significantly destroy the mechanical integrity of the substrate.

- 5 An exemplification of the range of pressures needed to compress the porous substrate will now be described, with reference to the following examples and comparative examples.

BEST MODE OF CARRYING OUT THE INVENTION:

EXAMPLE 1

- 10 A sheet of polysulfone substrate 150 μ m thick with pores of between 0.2 μ m and 0.5 μ m was dipped into a solution which was 1 wt% gelatine in water. The excess liquid was wiped from the outside of the substrate and the substrate dried in an oven to remove the water. The substrate was then pressed with a pressure of 100 MPa such that a compressed area in the form of a ring was formed on the substrate. The ring had
15 an internal diameter of 8 mm and an external diameter of 10 mm.

- 10 μ l of a solution of a dye (Rose Bengal) in water was dropped onto the substrate inside the ring. The dye solution was seen to spread to the inside edge of the compressed ring and then stop. No dye was visible outside the circular region defined by the compressed ring after approximately 1 hour, by which time the water in the dye
20 solution had evaporated.

COMPARATIVE EXAMPLE 1

- As in example 1 except the substrate was pressed with a pressure of 30 MPa. At this pressure there was some leakage of the dye to outside the defined area.

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EXAMPLE 2

As in example 1 except that the substrate was coated with approximately 60nm of platinum which was used as an electrode. Also, instead of a dye solution being dropped onto the substrate a solution containing ferrocyanide and ferricyanide was used, a potential applied to the platinum electrodes and the current recorded over time. After an initial higher current the current stayed constant for approximately 10 minutes, after which time the substrate started to dry out and lose electrical connection. This constant current indicated that no spreading of the solution outside the defined area had occurred.

10 COMPARATIVE EXAMPLE 2

As in example 1 except the substrate was pressed with a pressure of 55 MPa. Five defined areas were prepared. One showed some leakage of the dye outside the defined area, the other four showed no leakage.

EXAMPLE 3

15 As in example 2 except that a polyvinylidene difluoride substrate with approximately 0.2 μ m pores was used.

EXAMPLE 4

As in example 1 except the substrate was pressed with a pressure of 80 MPa. At this pressure there was no leakage of the dye outside the defined area.

20 COMPARATIVE EXAMPLE 4

As in example 1 except the substrate was not dipped into a gelatine solution. The pressure applied was 70 MPa. Four defined areas were prepared and the dye leaked to outside the defined area in all cases.

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COMPARATIVE EXAMPLE 5

As in example 1 except the substrate was not dipped into a gelatine solution and pressed with a pressure of 80 MPa. Five defined areas were prepared and the dye leaked to outside the defined area in four cases and no leakage was apparent in one case.

COMPARATIVE EXAMPLE 6

As in example 1 except the substrate was not dipped into a gelatine solution and pressed with a pressure of 100 MPa. Three defined areas were prepared and the dye leaked to outside the defined area in one case and no leakage was apparent in two cases.

Preferably, the membrane in the present invention is permeable to a fluid containing a first species to be analysed but substantially impermeable to a second species. An exemplification of this preferred embodiment of the invention will now be described with reference to the following example.

EXAMPLE A

A sheet of polysulfone 100 μ m thick with pores of 0.2 μ m was coated on one side with two 1mm strips of platinum. A defined electrode area was prepared in accordance with the method of Example 1. A sample of blood to be analysed was brought into contact with the substrate on the opposite side on which the sensing electrode was coated and within the defined area. It was found that the membrane was impermeable to the interfering species erythrocytes (II) in the blood but permeable to glucose or cholesterol (I). The first species, either glucose or cholesterol, could be analysed without interference from erythrocytes (II).

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It will be understood that in an electrochemical sensing device it is usual to employ two or three electrodes and in that case all the electrodes may extend into or pass through an area defined by a barrier or barriers according to the invention. For example, the compressed barrier may define a square through which two strip
5 electrodes pass. An area is thus defined on each electrode by the edges of that electrode and by the compressed barrier where the strip enters and leaves the square.

EXAMPLE B

In a highly preferred embodiment of the invention illustrated in Figure 11, substrate 10 is in the form of a strip having electrodes 1, 1A on opposite sides of the strip. Both electrodes 1, 1A extend longitudinally of the strip which has a plurality of defined square areas 4 spaced apart along the strip length, each area being defined by a boundary 8 formed by compression in accordance with the invention.

Each area 4 defines a predetermined area of electrodes 1 and 1A (shown crosshatched). In use a sample may be placed on an area 4 nearest the strip end.

15 Measurements may be made by connecting suitable apparatus with the electrodes at the opposite strip end in a manner that is conventional. Thereafter the "used" area may be cut from the strip and the next area 4 now closest to the strip end may be used for the next sample.

If desired, an absorbent strip may be provided on the side remote from the
20 sensor electrode to increase the sample volume and hence the signal or to reduce measuring times. Likewise if desired, one or more analytes might be contained within the volume of substrate bounded by compressed substrate 8.

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Although the invention has been described with reference to specific examples and Figures, it will be appreciated by those skilled in the art that the invention may be embodied in many other forms.

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CLAIMS:

1. A method for defining an area of a layer on a porous substrate comprising compressing a volume of the substrate to produce a compressed region which defines, or which in combination with an edge of the substrate or of the layer defines, a
5 boundary of the area and which substantially prevents the transport of material through or across its surface.
2. A method according to claim 1, wherein the layer is either attached to or in contact with the porous substrate or is a coating applied to the substrate.
3. A method according to claim 1 or claim 2, wherein the layer is an electrode
10 and the area being defined is an electrode area.
4. A method according to claim 3, wherein the electrode is formed on the surface of the substrate by a method selected from the group consisting of electroless plating, electroplating, evaporation, and sputtering.
5. A method according to claim 4, wherein the electrode is sputter deposited on
15 the surface of the substrate to form a continuous film.
6. A method according to claim 5, wherein the film thickness on the substrate is 10 to 200 nm.
7. A method according to claim 6, wherein the film thickness is 60 to 120 nm.
8. A method according to any one of claims 3 to 7, wherein the electrode is
20 made of materials selected from the group consisting of gold, silver, platinum, palladium, iridium, lead and alloys of those metals, carbon, carbon mixed with a binding material, and silver partially covered with a porous layer of an insoluble silver salt.

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9. A method according to claim 8, wherein the insoluble silver salt is silver chloride, silver bromide, silver iodide, silver ferrocyanide or silver ferricyanide.
10. A method according to any one of claims 1 to 9, further including a blocker in the substrate which assists in preventing transport of material in the compressed region.
11. A method according to claim 10, wherein the blocker is glucose, agar, gelatine or starch.
12. A method according to claim 10 or claim 11, wherein the blocker is loaded into the precompressed porous substrate using the steps of:
- 10 a) dissolving the blocker in a suitable solvent;
- b) wetting the substrate with the solution of the blocker; and then
- c) removing the solvent by evaporation.
13. A method according to any one of claims 1 to 12, wherein the substrate is made of a porous material selected from the group consisting of polymers or mixtures of polymers.
- 15 14. A method according to claim 13, wherein the polymers or mixtures of polymers consist of polysulfones, polyvinylidene halides, tetrafluoroethene, polyamides, polyimides, polyethylene, polypropylenes, polyacrylonitriles or polycarbonates.
- 20 15. A method according to claim 14, wherein the polyvinylidene halides are polyvinylidene difluorides.
16. A method according to any one of claims 1 to 15, wherein the thickness of the precompressed substrate is about 180 μ m or less.

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17. A method according to claim 16, wherein the thickness of the precompressed substrate is from 30 μ m to 150 μ m.
18. A method according to any one of claims 1 to 17, wherein the pore size of the substrate ranges from 10 kilodaltons cut-off (lower limit) to 5 microns.
- 5 19. A method according to claim 18, wherein the pore size of the substrate ranges from 0.1 μ m to 0.8 μ m.
20. A method according to claim 19, wherein the pore size of the substrate ranges from 0.2 μ m to 0.5 μ m.
21. A method for defining an area of a layer on a porous substrate which method
10 is substantially as herein described with reference to any one of the examples and/or accompanying figures but excluding the comparative examples.
22. An electrochemical sensing device comprising:
a porous substrate; and
an electrode on one side of the substrate; wherein a region of the substrate is
15 compressed to an extent which forms a barrier to migration of electrolyte within the substrate, the compressed region defining, or in combination with an edge of the substrate or the electrode defining, a zone on the electrode of predetermined area.
23. An electrochemical sensing device according to claim 22, wherein the electrode is formed on one side of the substrate by a method selected from the group
20 consisting of electroless plating, electroplating, evaporation, and sputtering.
24. An electrochemical sensing device according to claim 23, wherein the electrode is sputter deposited on the surface of the substrate to form a continuous film.

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25. An electrochemical sensing device according to claim 24, wherein the film thickness on the substrate is 10 to 200 nm.
26. An electrochemical sensing device according to claim 25, wherein the film thickness is 60 to 120 nm.
- 5 27. An electrochemical sensing device according to any one of claims 22 to 26, wherein the electrode is made of materials selected from the group consisting of gold, silver, platinum, palladium, iridium, lead and alloys of those materials, carbon, carbon mixed with a binding material, and silver partially covered with a porous layer of an insoluble silver salt.
- 10 28. An electrochemical sensing device according to claim 27, wherein the insoluble silver salt is silver chloride, silver bromide, silver iodide, silver ferricyanide or silver ferrocyanide.
29. An electrochemical sensing device according to any one of claims 22 to 28, wherein there are two or more electrodes and they are disposed on one side of the
- 15 substrate or on opposite sides of the substrate.
30. An electrochemical sensing device according to any one of claims 22 to 29, further including a blocker in the substrate which assists in preventing transport of material in the compressed region.
31. An electrochemical sensing device according to claim 30, wherein the
- 20 blocker is glucose, agar, gelatine or starch.
32. An electrochemical sensing device according to claim 30 or claim 31, wherein the blocker is loaded into the precompressed porous substrate using the steps of:

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- a) dissolving the blocker in a suitable solvent;
- b) wetting the substrate with the solution of the blocker; and then
- c) removing the solvent by evaporation.

33. An electrochemical sensing device according to any one of claims 22 to 32,
5 wherein the substrate is made of a porous material selected from the group consisting of polymers or mixtures of polymers.

34. An electrochemical sensing device according to claim 33, wherein the
polymers or mixtures of polymers consist of polysulfones, polyvinylidene halides,
tetrafluoroethene, polyamides, polyimides, polyethylene, polypropylene,
10 polyacrylonitrates or polycarbonates.

35. An electrochemical sensing device according to claim 34, wherein the
polyvinylidene halides are polyvinylidene difluorides.

36. An electrochemical sensing device according to any one of claims 22 to 35,
wherein the thickness of the precompressed substrate is about 180 μm or less.

15 37. An electrochemical sensing device according to claim 36, wherein the
thickness of the precompressed substrate is from 30 μm to 150 μm .

38. An electrochemical sensing device according to any one of claims 22 to 37,
wherein the pore size of the substrate ranges from 10 kilodaltons cut-off (lower limit)
to 5 microns.

20 39. An electrochemical sensing device according to claim 38, wherein the pore
size of the substrate ranges from 0.1 μm to 0.8 μm .

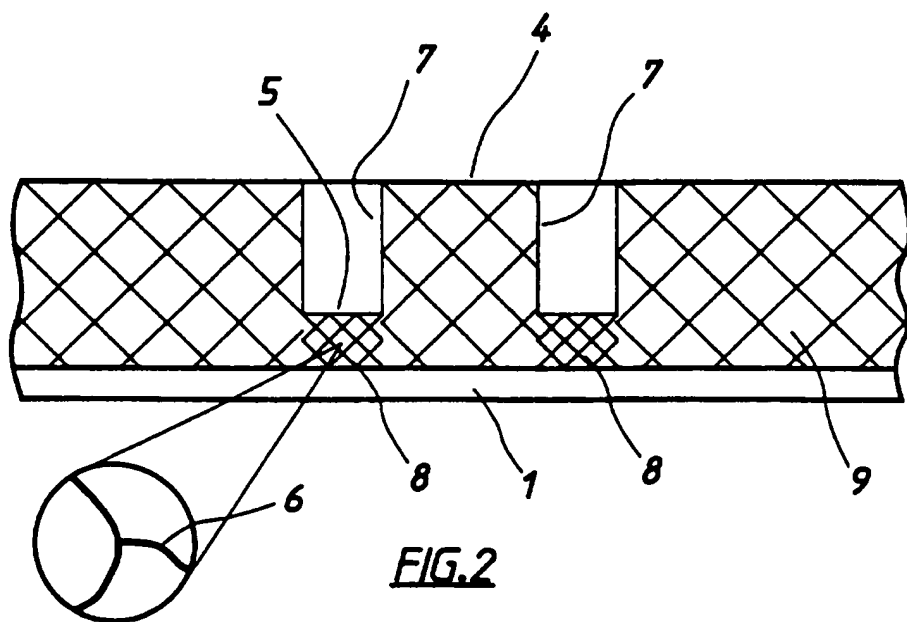
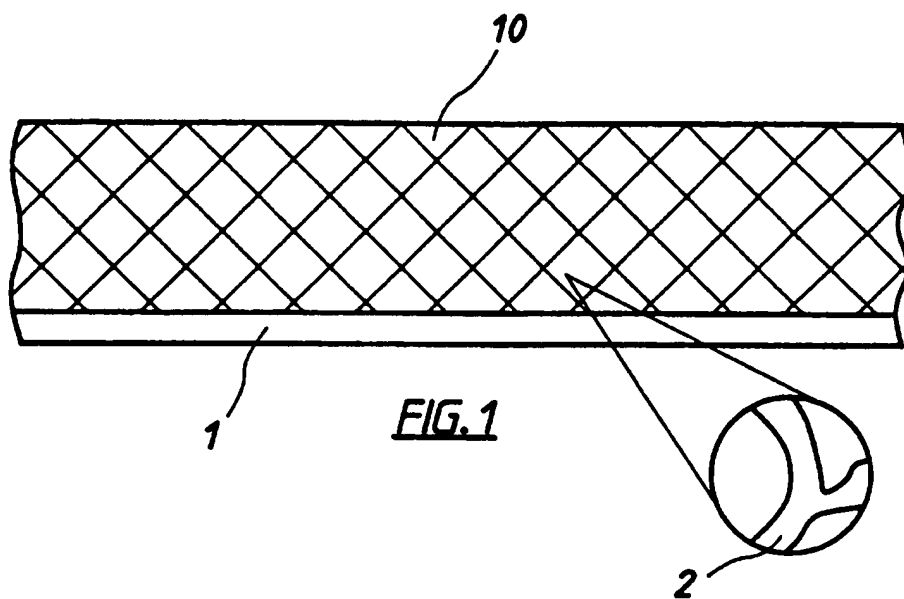
40. An electrochemical sensing device according to claim 39, wherein the pore
size of the substrate ranges from 0.2 μm to 0.5 μm .

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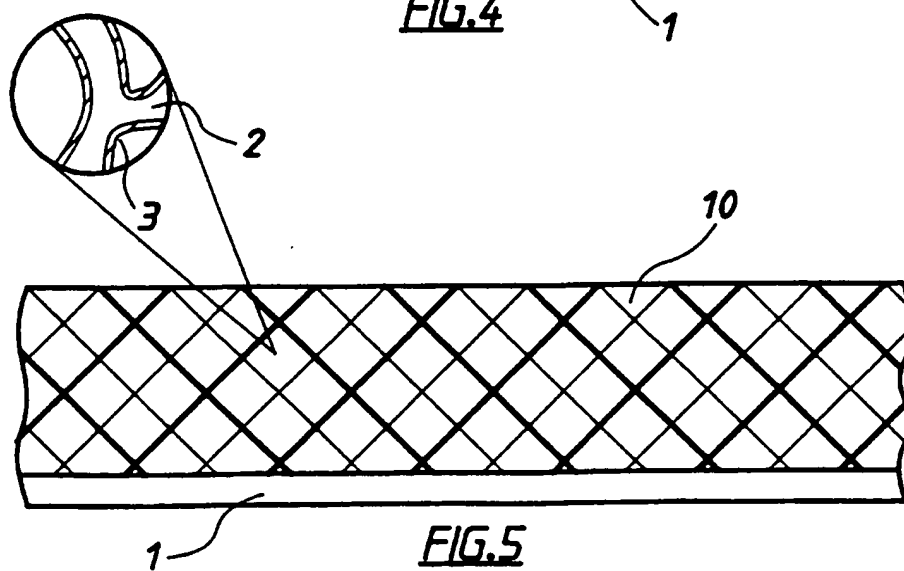
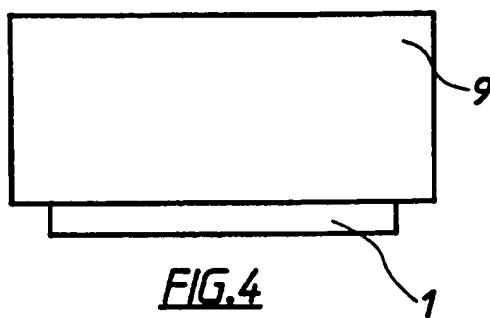
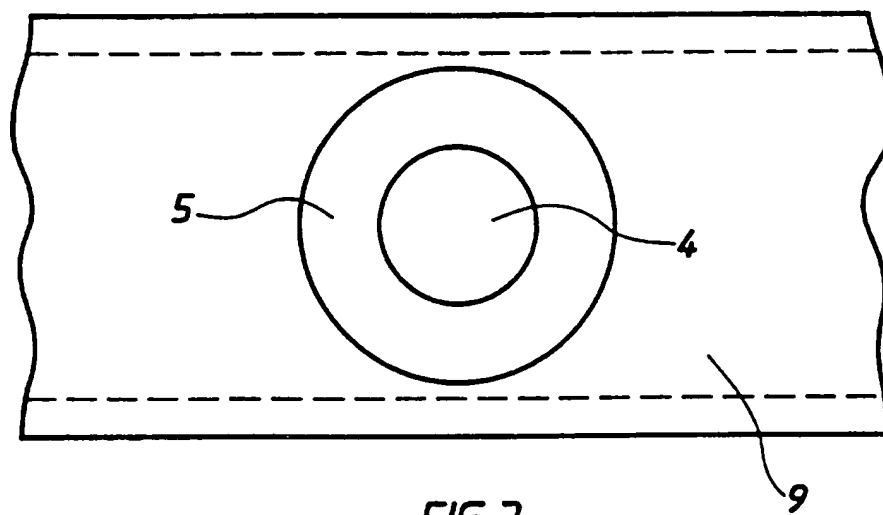
41. An electrochemical sensing device according to any one of claims 22 to 40,
wherein the porous substrate is a membrane that is permeable to a fluid containing a
first species to be analysed but substantially impermeable to a second species
contained in the fluid, the second species being of a kind which would interfere with
5 the electrochemical sensing of the first species.

42. An electrochemical sensing device substantially as herein described with
reference to any one of the examples and/or accompanying figures but excluding the
comparative examples.

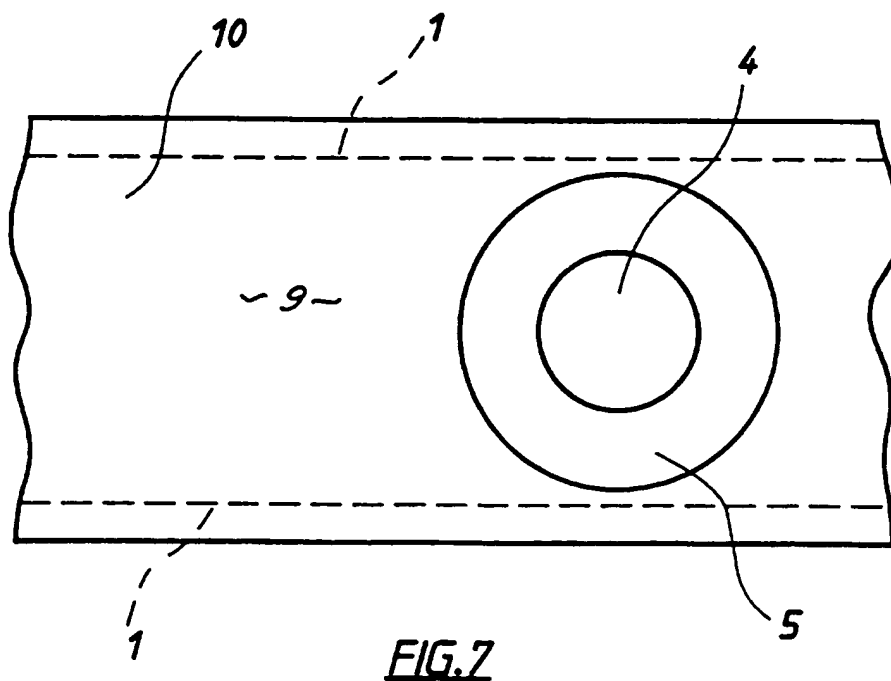
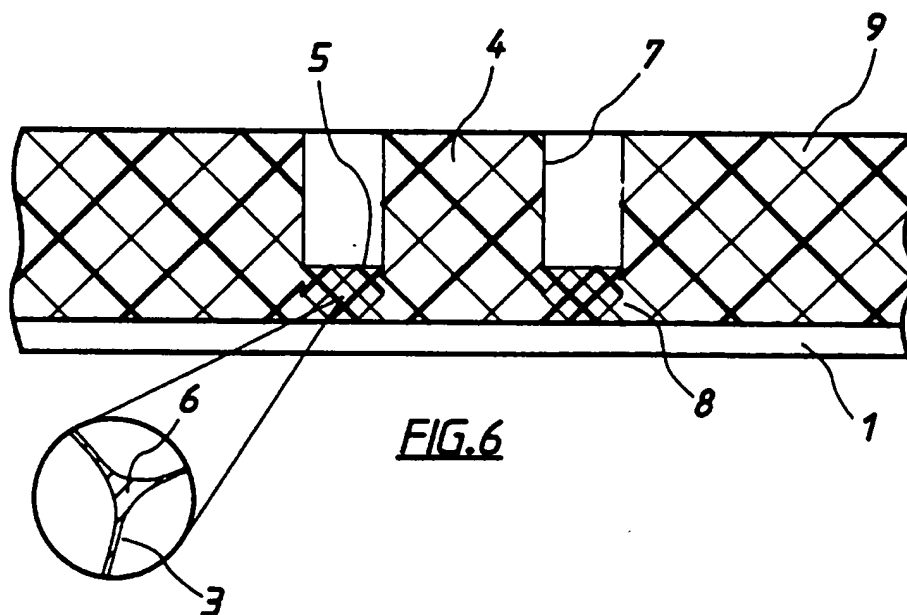
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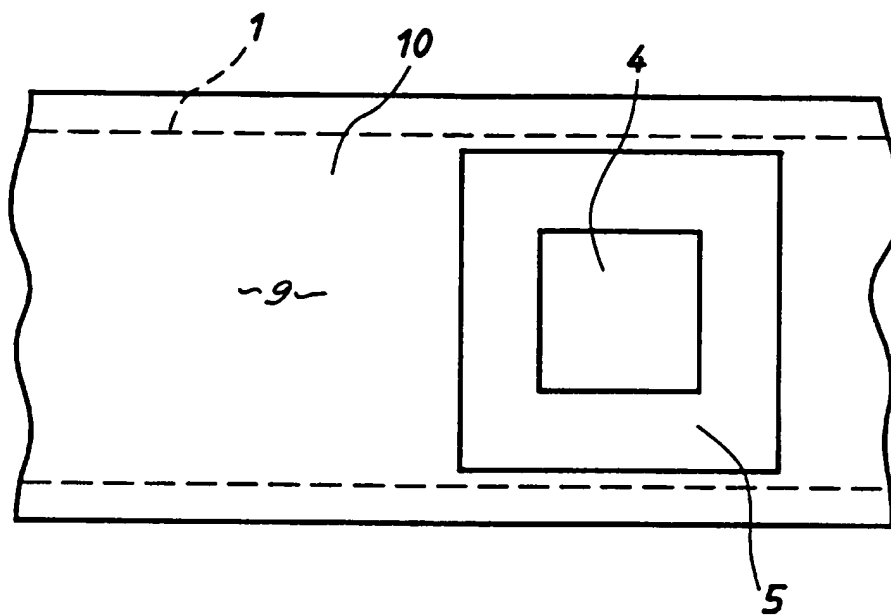


FIG. 8

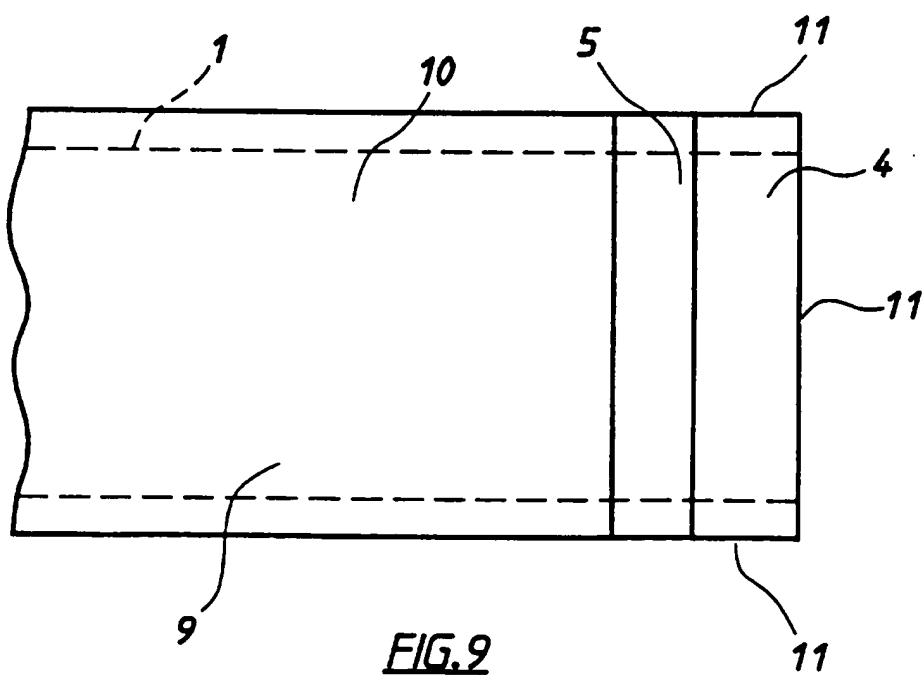


FIG. 9

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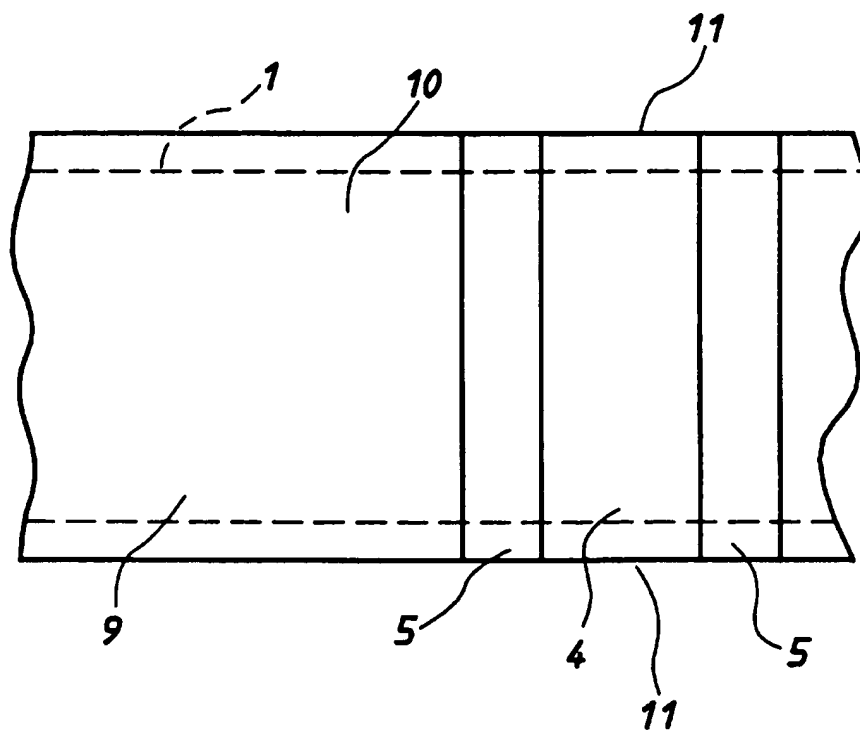


FIG. 10

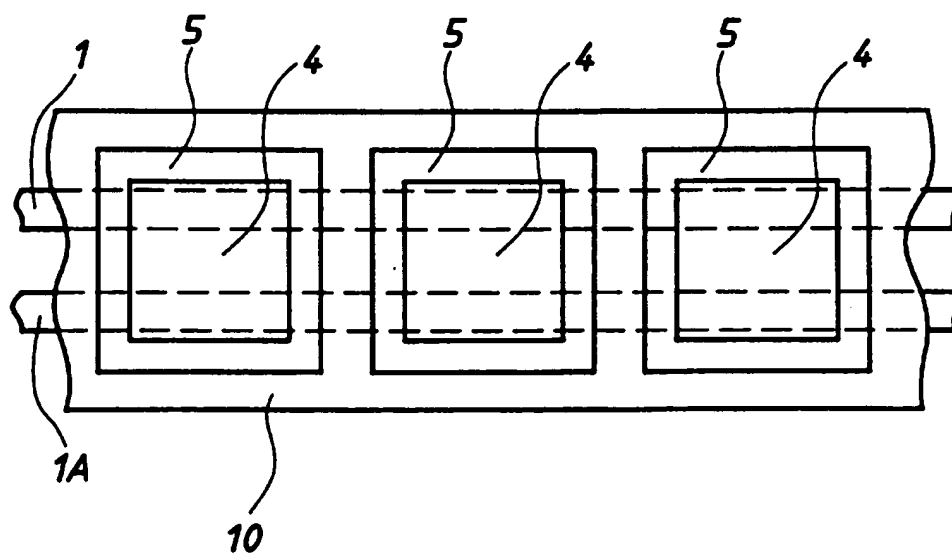


FIG. 11

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 96/00210

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl⁶: G01N 27/40, 27/403, B01D 61/38, 65/00, 69/00, C25B 11/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC G01N 27/31, 27/40, 27/403, B01D 61/38, 65/00, 67/00, 69/00, 69/06, C25B 11/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT, JAPIO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| A | Patent Abstracts of Japan, C-952, page 117 JP, 4-66112. A (UBE IND. LTD.) 2 April 1992 Abstract | 1 |
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| A | DE, 3103464, A (GKSS FORSCHUNGSZENT) 5 August 1982 Abstract and fig. | 1 |

☒ Further documents are listed in the continuation of Box C

☒ See patent family annex

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Date of the actual completion of the international search
5 June 1996

Date of mailing of the international search report

20TH JUNE 1996

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| C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No.
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This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent Document Cited in Search Report | | | | Patent Family Member | | | |
|--|--------|----|----------|----------------------|----------|----|--------------|
| EP | 266204 | AU | 80083/87 | AU | 80526/87 | JP | 63185404 |
| | | US | 4828705 | | | | |
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